



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 177 292 B1**

12

EUROPEAN PATENT SPECIFICATION

43 Date of publication of patent specification: 02.05.91 51 Int. Cl.⁵: **C22B 3/08, C22B 11/00**

21 Application number: 85306890.6

22 Date of filing: 27.09.85

- Supernatant ph
- Acid liq.

54 Process for the recovery of silver from a residue essentially free of elemental sulphur.

30 Priority: 27.09.84 CA 464180

43 Date of publication of application:
09.04.86 Bulletin 86/15

45 Publication of the grant of the patent:
02.05.91 Bulletin 91/18

64 Designated Contracting States:
BE DE FR GB IT NL

56 References cited:
DE-A- 2 323 186
US-A- 4 053 305
US-A- 4 063 933

73 Proprietor: Sherritt Gordon Limited
2800 Commerce Court West
Toronto, Ontario(CA)

72 Inventor: Genik-Sas-Berezowsky, Roman M.
15115 - 84th Street
Edmonton Alberta(CA)
Inventor: Weir, Donald R.
10228 - 109th Street
Fort Saskatchewan Alberta(CA)

74 Representative: Lambert, Hugh Richmond et al
D. YOUNG & CO. 10 Staple Inn
London, WC1V 7RD(GB)

EP 0 177 292 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to the recovery of silver from residues essentially free of elemental sulphur obtained by acidic pressure oxidation leaching of iron containing sulphidic material, for example refractory auriferous iron containing sulphidic material.

It is known to leach iron containing sulphidic materials, for example ores or concentrates, under pressurized oxidizing conditions in aqueous sulphuric acid solution in processes for the recovery of non-ferrous metal values in the material, for example copper, zinc, nickel, silver and gold. Copper, zinc and nickel values are dissolved in such leaching, and can be subsequently recovered from the resultant leach solution. Silver and gold remain in the leach residue and accordingly have to be recovered therefrom.

There are various ways of recovering gold and silver from an acidic pressure oxidation leach residue, for example by recovery treatment including cyanidation or ammonium thiosulphate leaching. It is known that, although satisfactory gold recovery can be obtained by directly treating acidic pressure oxidation leach residues in an appropriate gold recovery process, silver recovery is frequently very poor. It has been believed that the poor silver recovery was due to the presence of elemental sulphur in the residue formed during the acidic pressure oxidation leach, and accordingly attempts have been made to remove elemental sulphur from such residues before carrying out silver recovery treatment, for example as described in United States Patent No. 4,063,933 (Peters) issued December 20, 1977 in which the residue is subjected to a lime leach to remove elemental sulphur, with the resultant solids being separated from the solution before being subjected to silver and lead recovery steps. In other words, the teaching of the prior art has been to remove elemental sulphur from the acidic pressure oxidation leach residue before attempting silver recovery, with such sulphur removal usually involving treatment with lime and subsequent liquid-solids separation.

Another probable cause of poor silver recovery from pressure oxidation residues is the association of silver in a refractory iron compound formed by hydrolysis and subsequent precipitation of iron during the acidic pressure oxidation leach. Such as refractory iron compounds, which effectively inhibit silver recovery therefrom, comprise hematite, basic ferric sulphate, ferric arsenate and various jarosites depending upon the nature of the starting material and the acidic pressure oxidation leach conditions.

In accordance with the present invention, it has been found that these two problems can be solved, and that recovery of silver, and optionally gold, is improved by a) conducting the pressurised oxidation leach under conditions which provide an essentially elemental sulphur-free residue, and b) before the actual silver recovery treatment, forming a slurry of the essentially elemental sulphur-free residue with lime at a temperature of at least about 80°C, advantageously above about 90°C, to raise the pH of the slurry to at least about 9, preferably to at least about 10, maintaining the slurry at said temperature for from about 0.5 to about 4 hours, and subjecting the resultant slurry to silver recovery treatment, preferably without prior liquid-solids separation.

According to a preferred aspect of the invention, the essentially elemental sulphur-free residue is formed into a slurry at a temperature of at least about 80°C with lime to raise the pH to at least about 9 and with an alkali carbonate to raise the pH to at least about 10, again with the resultant slurry being then subjected to silver recovery treatment, preferably without prior liquid-solids separation. Also, a liquid-solids separation step between the alkaline treatment and the silver recovery treatment may not be necessary.

Generally the condition required to provide an essentially elemental sulphur-free residue, i.e. containing less than 10% elemental sulphur, based on the total sulphur content of the sulphidic material fed to the pressurised oxidation leach, comprise treating the sulphidic material over a period of from 1-3 hours with aqueous sulphuric acid containing from 5 to 40 g/L sulphuric acid at a temperature in the range 160 to 200°C, at a pulp density of from 5 to 50% solids, and a pressure of from 1000 to 5000 kPa.

By maintaining the conditions as described, it is found that the silver is effectively released from its association with the refractory iron compounds, and the necessity of an elemental sulphur removal step prior to recovery of the silver (and probably also gold) from the oxidised residue is eliminated.

One embodiment of the invention will now be described, by way of example, with reference to the accompanying drawing in which Figures 1 and 2 show flow sheets of processes for the recovery of gold and silver from auriferous refractory iron containing sulphidic ore or concentrate.

Referring first to Figure 1, auriferous refractory iron containing sulphidic ore or concentrate which is treated in this embodiment contains in the case of ore from about 3 to about 30 g/t gold, from about 15 to about 150 g/t silver, from about 1 to about 15% iron, from about 1 to about 10% sulphur by weight, and up to about 4% arsenic. In the case of concentrate, these may be from about 10 to about 240 g/t gold, from about 30 to about 300 g/t silver, from about 0.1 to about 25% arsenic, from about 10 to about 40% iron and from about 10 to about 45% sulphur.

After grinding to a suitable size, for example 70% minus 325 mesh Tyler screen (less than 45 μm), the ore or concentrate is subjected to an acid pressure oxidation step 12 where the ore or concentrate is treated in aqueous sulphuric acid solution containing from about 5 to about 40 g/L sulphuric acid, at a temperature of from about 160 to about 200 °C, a pulp density of from about 5 to about 50% solids, and a total pressure of from about 1000 to about 5000 kPa. The retention time may be from about 1 to about 3 hours. Under such conditions, sulphur values in the ore or concentrate are converted to sulphate form with essentially no elemental sulphur being present in the end residue. In other words, the residue would contain less than 10% and preferably less than 0.5% by weight of elemental sulphur compared to the sulphur in the ore or concentrate.

The slurry then proceeds to a thickener 14 from which the leach solution is treated as desired, for example for recovery of dissolved metal values therein, and at least partially recycled to the pressure oxidation step 12 to provide aqueous sulphuric acid solution therefor.

The solids slurry containing the gold and silver proceeds from thickener 14 to an alkaline treatment step 16 in accordance with the invention. Lime slurry is added to raise the pH to about 10, and then sodium carbonate is added to raise the pH to about 10.5, with the temperature being maintained at at least 80 °C. The time taken for the alkaline treatment step 16 may be from about 1 to about 2 hours to ensure adequate digestion of the residue in the alkaline slurry.

After the alkaline treatment step 16, the resultant slurry is cooled and proceeds to an appropriate gold and silver recovery step 18, which may comprise recovery by cyanidation in known manner.

Figure 2 shows an alternative flow sheet in which a gold recovery step 18a is carried out in any suitable manner, such as by cyanidation, before the alkaline pretreatment step 16, which is followed after cooling by silver recovery step 18b.

Various tests made in connection with the invention will now be described.

25

EXAMPLE 1

Refractory ore containing 6.3 g/t Au, 25.5 g/t Ag, 6.89% Fe and 4.77% sulphur was subjected to an acidic pressure oxidation step 12 as a 32% solids slurry at a temperature of 185 °C, an oxygen partial pressure of 700 kPa, a starting acidity of 5 g/L H_2SO_4 , and a retention time of 2 hours. The residue was filtered and washed, and was found to contain 5.87 g/t Au, 24.4 g/t Ag, and less than 0.1% elemental sulphur.

A series of cyanidation tests on residue samples was conducted in accordance with the teaching of the prior art at 25 °C for 24 hours over a pH range of 10-12, the pH adjustment being carried out at 25 °C with lime slurry, and with subsequent liquid-solids separation. A further test was carried out for 72 hours at pH 10.5. The results are shown in Table 1.

TABLE 1

40

pH	Time (h)	Assays (g/t)		Extractions (%)	
		Au	Ag	Au	Ag
10.0	24	0.23	23.7	96.1	2.9
10.5	24	0.19	22.0	96.8	9.8
10.5	72	0.21	16.5	96.5	32.4
11.0	24	0.20	25.8	96.6	0.0
11.5	24	0.19	29.2	96.8	0.0
12.0	24	0.24	23.0	96.0	5.7

55

The results show that the gold extraction was substantially unaffected over the pH range, and that silver extractions were poor, although silver recovery was somewhat improved by extending the time to 72 hours.

EXAMPLE 2

Tests on residue samples were then carried out in accordance with the invention, i.e. treatment with lime, either alone or followed by treatment with sodium carbonate, at a temperature of at least about 80 °C, and with subsequent cyanidation being carried out on the resultant slurry, i.e. with no prior liquid-solids separation. The results are shown in Table 2.

TABLE 2

Alkaline Treatment				Cyanidation Residues	
Temp(°C)	System	pH	Time (hr)	Ag (g/t)	% Extn Ag
80	Ca(OH) ₂ /Na ₂ CO ₃	10.5	2	<2	>92
80	Ca(OH) ₂	11.0	2	<2	>92
95	Ca(OH) ₂	10.5	2	<2	>92
95	Ca(OH) ₂ /Na ₂ CO ₃	10.5	1	<2	>92

The advantages of the invention are therefore readily apparent from Table 2 with the silver recovery being increased to over 90%, far higher than the values shown in Table 1. It was found that gold extraction was also improved.

EXAMPLE 3

A refractory auriferous arsenopyrite concentrate, containing 63.5 g/t Au, 36.0 g/t Ag, 8.8% As, 24.1% Fe and 22.1% S, was reground to 94% minus 44 µm. Conventional cyanidation of the reground concentrate extracted 32.0% Au and 30.3% Ag.

The concentrate was pressure oxidized in a continuous six compartment autoclave, at 190 °C, 1650 kPa total pressure, and a nominal retention time of 2.5 h. Conventional cyanidation of samples of the oxidized concentrate produced during the run extracted in the range of 93.5 to 95.5% Au, and 0 to 12% Ag. Thus, although the pressure oxidation was effective in liberating refractory gold, the silver was rendered more refractory.

The slurry of oxidized concentrate discharged from the autoclave was subjected to two stages of washing in a CCD circuit, to remove dissolved arsenic, iron, sulphate and cyanicides liberated in the pressure oxidation. The second wash thickener underflow was subjected to pH adjustment and pretreatment in a continuous circuit comprising four stirred tanks in series. The slurry, containing 60% by weight solids, was adjusted to pH 10.8 with 180 kg CaO per tonne of oxidized solids, and diluted with water to 35% solids. The pretreatment was conducted in the second and third tanks at 90 to 95 °C. The slurry was then cooled to 40 °C in the fourth tank, before proceeding to cyanidation. Retention time in the pretreatment tanks was 1.8 h each. The pretreated slurry was subjected to a single stage of leaching, in a stirred tank, at 40 °C, with a retention time of 4.5 h. Gold and silver extractions at this point were 97.0 and 81.1% respectively. The leached slurry was then further processed through a carbon in leach solution, comprising twelve stages, each with a 1 h retention, for additional leaching and gold and silver recovery by adsorption onto carbon. Extractions after three stages were 97.6% Au and 81.7% Ag. After the twelfth stage, the extractions were 97.8% Au and 82.7% Ag.

Claims

1. A process for the recovery of silver and optionally gold from sulphidic materials containing iron, silver and possibly gold, which comprises leaching the sulphidic material with an acid leach under pressure oxidation conditions thereby to convert sulphur values in the sulphidic material to sulphate and to produce an acid leach solution containing said iron and a silver or silver and gold-containing solids residue, treating said solids residue to a silver recovery process to recover the silver therefrom and, optionally also to a gold recovery process, said silver recovery process comprising subjecting said solids residue initially to an alkaline lime leach, prior to further treatment of said solids residue to recover said silver and optionally said gold, characterised in that the pressurised oxidation leach is performed by treating the sulphidic material over a period of from 1-3 hours with aqueous sulphidic acid containing from 5 to 40 g/L sulphuric acid at a temperature in the range 160 to 200 °C, at a pulp density of from 5 to 50% solids, and a total pressure of from 1000 to 5000 kPa thereby to produce said leach solution and an essentially elemental sulphur-free solids residue containing elemental sulphur in an amount of less than 10%, based on the total sulphur content of the sulphidic material fed to the pressurised oxidation leach, and in that the silver recovery process comprises forming a slurry of the said essentially elemental sulphur-free solids residue with said alkaline lime leach at a pH of at least 9, and holding the slurry at a temperature of at least 80 °C for a period of from 0.5 to 4 hours prior to the recovery of said silver from the slurry.
2. A process according to claim 1, wherein the elemental sulphur content of said essentially elemental sulphur-free silver-containing solids residue is less than 0.5% as compared with the sulphur content of the material originally subjected to acidic pressure oxidation leaching.
3. A process according to claim 1 or 2, wherein, prior to the recovery of the silver from said slurry, the pH of the slurry is raised to at least 10 by the addition thereto of an alkali metal carbonate.
4. A process according to claim 3, wherein the alkali carbonate used is sodium carbonate.
5. A process according to any one of the preceding claims, wherein the silver is recovered from the lime treated slurry by cyanidation.
6. A process according to any one of the preceding claims, wherein the lime treated slurry is subjected to silver recovery treatment without liquid-solids separation.
7. A process according to any one of the preceding claims, wherein the sulphidic material subjected to said pressure oxidation leach also contains gold, and the essentially elemental sulphur-free residue from the oxidation leach is treated to recover said gold as well as said silver.
8. A process according to claim 7, wherein the essentially sulphur-free residue from the oxidation leach is treated to separate the gold therefrom before treating the residue with said lime in preparation for the recovery of said silver.
9. A process according to claim 7 or 8, wherein the gold is recovered by cyanidation.

Revendications

1. Un procédé de récupération de l'argent et éventuellement de l'or des matières sulfurées contenant du fer, de l'argent et éventuellement de l'or, qui comprend l'extraction de la matière sulfurée par un milieu acide dans des conditions oxydantes sous pression pour convertir les produits contenant du soufre dans la matière sulfurée en sulfate et pour produire une solution d'extraction acide contenant ledit fer et un résidu solide contenant de l'argent ou de l'argent et de l'or, le traitement de ce résidu solide dans un procédé de récupération de l'argent pour récupérer l'argent dudit résidu et éventuellement également dans un procédé de récupération de l'or, ledit procédé de récupération de l'argent consistant à soumettre ledit résidu solide initialement à une extraction alcaline à la chaux, avant de procéder au traitement dudit résidu solide pour récupérer ledit argent et éventuellement ledit or, caractérisé en ce que l'extraction par oxydation sous pression est conduite en traitant la matière sulfurée pendant une période de 1-3 h par l'acide sulfuré aqueux contenant de 5 à 40 g/l d'acide

- 5 sulfurique à une température comprise dans l'intervalle de 160 à 200 °C, à une densité de pâte de 5 à 50 % de solides, et à une pression totale de 1 000 à 5 000 kPa afin de produire ladite solution d'extraction et un résidu solide essentiellement exempt de soufre élémentaire, contenant ce soufre élémentaire en quantité inférieure à 10 %, basée sur la teneur totale en soufre de la matière sulfurée
- 10 alimentée dans l'étape d'extraction par oxydation sous pression, et en ce que le procédé de récupération de l'argent comprend la formation d'une bouillie dudit résidu solide essentiellement exempt de soufre élémentaire avec ladite solution d'extraction alcaline contenant de la chaux à un pH d'au moins 9, et le maintien de la bouillie à une température d'au moins 80 °C pendant une période de 0,5 à 4 h avant la récupération de l'argent à partir de la bouillie.
- 15 2. Un procédé selon la revendication 1, selon lequel la teneur en soufre élémentaire dudit résidu solide contenant de l'argent essentiellement exempt de soufre élémentaire est inférieure à 0,5 % par rapport à la teneur en soufre de la matière soumise initialement à l'extraction à l'acide dans des conditions oxydantes sous pression.
- 20 3. Un procédé selon la revendication 1 ou 2, selon lequel avant la récupération de l'argent à partir de ladite bouillie, le pH de la bouillie est porté à au moins 10 par addition d'un carbonate de métal alcalin.
4. Un procédé selon la revendication 3, selon lequel le carbonate alcalin utilisé est le carbonate de sodium.
- 25 5. Un procédé selon l'une quelconque des revendications précédentes, selon lequel l'argent est récupéré à partir de la bouillie traitée à la chaux par cyanuration.
6. Un procédé selon l'une quelconque des revendications précédentes, selon lequel la bouillie traitée à la chaux est soumise à un traitement de récupération de l'argent sans séparation liquide-solides.
- 30 7. Un procédé selon l'une quelconque des revendications précédentes, selon lequel la matière sulfurée soumise à ladite extraction par oxydation sous pression contient également de l'or, et le résidu essentiellement exempt de soufre élémentaire provenant de l'extraction par oxydation est traité pour récupérer ledit or ainsi que ledit argent.
8. Un procédé selon la revendication 7, selon lequel le résidu essentiellement exempt de soufre provenant de l'extraction par oxydation est traité pour séparer l'or avant de traiter le résidu par la chaux en vue de la récupération de l'argent.
- 35 9. Un procédé selon la revendication 7 ou 8, selon lequel l'or est récupéré par cyanuration.

40 Ansprüche

1. Verfahren zur Gewinnung von Silber und gegebenenfalls Gold aus sulfidischen Materialien, die Eisen, Silber und möglicherweise Gold enthalten, bei dem das sulfidische Material mit einer Säurelaugung unter Druck-Oxidationsbedingungen gelaugt wird, um dadurch Schwefelanteile aus dem sulfidischen
- 45 Material zu Sulfat umzuwandeln und eine das Eisen enthaltende saure Laugungslösung sowie einen Silber bzw. Silber und Gold enthaltenden Feststoff-Rückstand zu erzeugen, und bei dem der Feststoff-Rückstand in einem Silber-Gewinnungsprozeß zur Gewinnung des Silbers daraus und gegebenenfalls auch in einem Gold-Gewinnungsprozeß behandelt wird, wobei in dem Silber-Gewinnungsprozeß der Feststoff-Rückstand vor seiner Weiterbehandlung zum Zweck der Silber- und gegebenenfalls Goldge-
- 50 winnung zunächst einer alkalischen Kalk-Laugung unterzogen wird, dadurch gekennzeichnet, daß die Druck-Oxidationslaugung durch Behandlung des sulfidischen Materials während einer Zeitdauer von 1 bis 3 Stunden mit wässriger Schwefelsäure mit einem Gehalt von 5 bis 40 g/l Schwefelsäure, bei einer Temperatur im Bereich von 160 bis 200 °C, bei einer Schlämmdichte von 5 bis 50 % Feststoff
- 55 und bei einem Gesamtdruck von 1.000 bis 5.000 kPa ausgeführt wird, um dadurch die genannte Laugungslösung und einen im wesentlichen von elementarem Schwefel freien Feststoff-Rückstand mit einem Elementarschwefel-Gehalt von unter 10%, bezogen auf den Gesamt-Schwefelgehalt des der Druck-Oxidationslaugung zugeführten sulfidischen Materials, zu erzeugen, und daß in dem Silber-

Gewinnungsprozeß aus dem im wesentlichen von Elementarschwefel freien Feststoff-Rückstand mit der alkalischen Kalklauge mit einem pH-Wert von mindestens 9 eine Aufschlämmung gebildet wird, welche während einer Zeitdauer von 0,5 bis 4 Stunden vor der Silbergewinnung daraus auf einer Temperatur von zumindest 80° C gehalten wird.

- 5
2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß der Elementarschwefel-Gehalt des von Elementarschwefel im wesentlichen freien, silberhaltigen Feststoff-Rückstands weniger als 0,5% im Vergleich mit dem Schwefelgehalt des ursprünglich der
10 Säure-Druck-Oxidationslaugung unterzogenen Materials beträgt.
3. Verfahren nach Anspruch 1 oder 2,
dadurch gekennzeichnet,
daß vor der Silbergewinnung aus der Aufschlämmung der pH-Wert der Aufschlämmung durch Zugabe
15 eines Alkalimetall-Karbonats auf mindestens 10 angehoben wird.
4. Verfahren nach Anspruch 3,
dadurch gekennzeichnet,
daß das verwendete Alkalimetall-Karbonat Natriumkarbonat ist.
20
5. Verfahren nach einem der vorangehenden Ansprüche,
dadurch gekennzeichnet,
daß das Silber aus der mit Kalk behandelten Aufschlämmung durch Cyanidierung gewonnen wird.
- 25 6. Verfahren nach einem der vorangehenden Ansprüche,
dadurch gekennzeichnet,
daß die mit Kalk behandelte Aufschlämmung einer Silbergewinnungs-Behandlung ohne Flüssig/Feststoff-Trennung unterzogen wird.
- 30 7. Verfahren nach einem der vorangehenden Ansprüche,
dadurch gekennzeichnet,
daß das der Druck-Oxidationslaugung unterzogene sulfidische Material auch Gold enthält und der von Elementarschwefel im wesentlichen freie Rückstand aus der Oxidationslaugung sowohl zum Zweck der Gold- als auch Silbergewinnung behandelt wird.
35
8. Verfahren nach Anspruch 7,
dadurch gekennzeichnet,
daß der von Elementarschwefel im wesentlichen freie Rückstand aus der Oxidationslaugung zur Abscheidung des Goldes daraus behandelt wird, bevor der Rückstand mit Kalk als Vorbereitung für die Silbergewinnung behandelt wird.
40
9. Verfahren nach Anspruch 7 oder 8,
dadurch gekennzeichnet,
daß das Gold durch Cyanidierung gewonnen wird.
45

50

55

FIG.1.

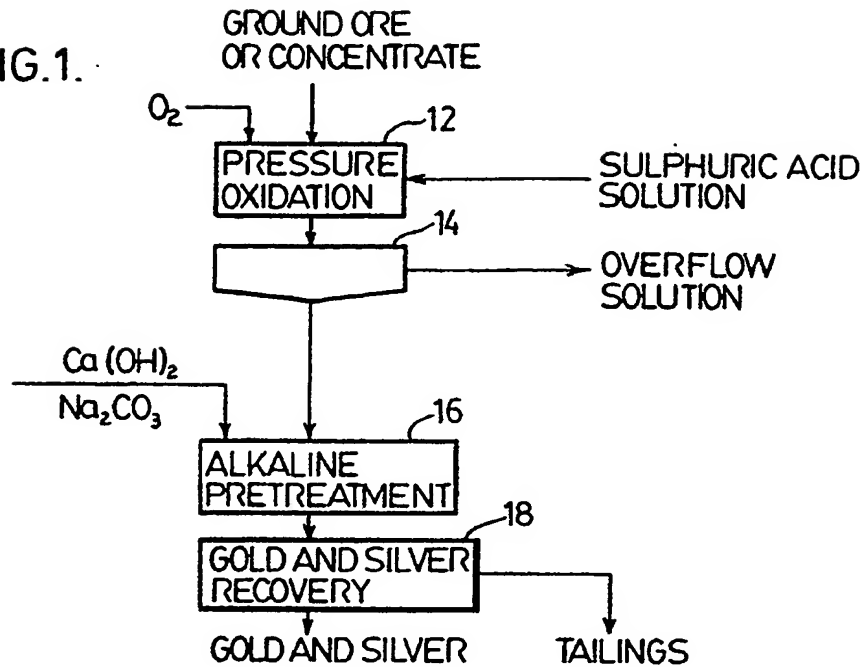


FIG.2.

